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(54) SULFUR REMOVAL USING FERROUS CARBONATE ABSORBENT

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(57) ABSTRACT

Finely divided ferrous carbonate absorbent, siderite granules or absorbent particles made by mixing, agglomerating and shaping finely powdered ferrous carbonate, preferably siderite, in combination with minor effective amounts of water or an optional binder, followed by drying, are used to treat and significantly reduce concentrations of hydrogen sulfide, carbonyl sulfide, organic disulfides, mercaptans and other sulfurous compounds and contaminants in gaseous and liquid fluid streams such as natural gas, light hydrocarbon streams, crude oil, acid gas mixtures, carbon dioxide gas and liquid streams, anaerobic gas, landfill gas, geothermal gases and liquids, and the like.

37 Claims, No Drawings

SULFUR REMOVAL USING FERROUS CARBONATE ABSORBENT

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to an absorbent composition useful for removing sulfur-containing compounds from a variety of fluids, and particularly from liquid and gaseous hydrocarbons and carbon dioxide. The absorbent primarily comprises ferrous carbonate, desirably obtained from the mineral siderite, and is used for removing hydrogen sulfide, mercaptans, dimethyl disulfide and other sulfur-containing compounds from gaseous hydrocarbon streams, light liquid hydrocarbon streams such as natural gas liquids ("NGL"), crude oil, acid-gas mixtures, carbon dioxide gas and liquid, anaerobic gas, landfill gas, geothermal gas, and the like. Methods for making and using the absorbent for sulfur removal are also disclosed.

2. Description of Related Art

Because of the noxious, toxic and corrosive nature of sulfur-containing compounds, many different products and methods have previously been disclosed for use in removing such compounds from liquid and gaseous streams. One such commercially available product is SULFATREAT® brand particulate reactant that is said to be useful for removing hydrogen sulfide and other sulfur contaminants from gases and liquids including, for example, hydrocarbon fuels and geothermal steam for sale to producers of natural gas and the like. SULFATREAT® is a federally registered trademark of M-I L.L.C. of Houston, Tex. and, in stylized form, of Gas Sweetener Associates, Inc. of Chesterfield, Mo. The SULFATREAT® material has a proprietary formulation but is believed to comprise primarily ferric oxide particles having a high surface area. Iron sponge is another commercially available material composed of ferric oxide distributed on wood chips that is being used for sulfur removal in industrial processes.

Other iron-containing compositions and methods for removing sulfur from gas and liquid streams are disclosed, for example, in U.S. Pat. Nos. 4,008,775; 4,344,842; 4,366,131; 4,476,027; 4,705,638; 4,956,160 and 5,948,269. U.S. Pat. No. 5,948,269, for example, discloses a process for the removal of dissolved hydrogen sulfide and other malodorous compounds from aqueous liquid or sludge waste systems such as found in sewage collection and treatment works; industrial and commercial waste systems, natural and man-made polluted impoundments or waterways, and septic systems, by use of "alkaline iron." As used in U.S. Pat. No. 5,948,269, "alkaline iron" refers to an alkali with a variety of iron compounds including ferrous carbonate.

SUMMARY OF THE INVENTION

The absorbent and method disclosed herein are particularly effective for absorbing hydrogen sulfide, mercaptans, dimethyldisulfide and other sulfur-containing compounds from natural gas, light hydrocarbon streams such as natural gas liquids, crude oil, acid gas mixtures, carbon dioxide gas and liquid, anaerobic gas, landfill gas, geothermal and other sulfur-containing streams. According to a preferred embodiment of the invention, the subject absorbent comprises ferrous carbonate, most preferably siderite granules or powdered siderite that is extruded or otherwise aggregated, compacted or formed into pellets, prills or spheroids using a minor effective amount of moisture and, optionally, a binder such as calcium aluminate cement or another similarly effective material.

According to another embodiment of the invention, an absorbent bed is disclosed for use in removing sulfur from gas, liquid or mixed gas and liquid streams. Examples of sulfur-containing compounds removed by the absorbent include hydrogen sulfide, mercaptan-containing compounds, organic disulfides and carbonyl sulfide. The absorbent bed desirably comprises a three-dimensional array of closely spaced pellets, prills, or otherwise-manufactured aggregates comprising from about 50 to about 100 weight percent ferrous carbonate, most preferably in the form of particulate siderite (90% through 100 mesh) aggregated using a binder comprising from about two to about ten weight percent calcium aluminate cement. According to a particularly preferred embodiment of the invention, the absorbent comprises dried extrudates containing about 95 weight percent siderite and about 5 weight percent calcium aluminate cement.

According to another embodiment of the invention, an absorbent material is made by mixing about 95 parts by weight particulate siderite (90% through 100 mesh), about 5 parts calcium aluminate cement, and about 20 parts water; compacting the mixture by extrusion or otherwise to produce larger particles, pellets or prills, and thereafter drying the absorbent for a sufficient time to reduce the moisture content to a moisture level less than about three weight percent. According to a particularly preferred embodiment of the invention, the absorbent pellets have a diameter of about 3/16 inch, a length of about 5/16 inch, and are dried at about 120° F. for about four hours.

According to another embodiment of the invention, sulfur is removed from a liquid, gas, or mixed gas and liquid stream comprising sulfur-containing compounds by causing the stream to pass through an absorbent bed consisting essentially of particulate material comprising from about 70 to about 100 weight percent ferrous carbonate, preferably in the form of aggregated particulate siderite. The absorbent bed most preferably comprises a plurality of pellets comprising from about 70 to about 100 weight percent ferrous carbonate in combination with an amount of a binder such as calcium aluminate cement that is sufficient to hold the absorbent in a desired physical configuration for a desired service life. It will be appreciated by those of ordinary skill in the art upon reading this disclosure that the amount of the inventive absorbent that is needed in the absorbent bed will depend upon factors such as the absorbent particle size, the bed density, the effective surface area of the absorbent particles, the amount of ferrous carbonate in the absorbent that is available to absorb the sulfur-containing compounds, and the temperature, pressure, velocity and residence time of the gas or liquid stream being treated as it passes through the bed.

According to another embodiment of the invention, a method is disclosed for removing hydrogen sulfide evolved during natural gas drilling operations, the method comprising adding to a drilling mud used in said drilling operations from about 40 to about 400 pounds of a finely ground particulate absorbent (particles passing through a 100 mesh screen), preferably comprising from about 50 to about 90 weight percent ferrous carbonate, per ton of drilling mud. No binder is needed or desirable when the finely ground ferrous carbonate is added to drilling mud according to this embodiment of the invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Applicant has discovered that ferrous carbonate, preferably in the form of the mineral siderite, is an excellent absorbent of hydrogen sulfide, carbonyl sulfide, organic disulfides, mercaptans and other sulfur-containing compounds that are present in various naturally occurring or synthesized gases and liquids, and particularly, in gaseous and liquid hydrocarbons and carbon dioxide. Siderite predominantly comprises ferrous carbonate, and is usually found naturally in combination with some calcium, magnesium or manganese. For use in the compositions and various methods of the invention, the siderite can be sourced in the form of chunks, granules, or finely divided powder. If sourced in chunks, the chunks are desirably reduced to granules of a suitable size or powdered prior to use. For use in bed applications, extrudates, as described below, or comparably sized siderite granules obtained from natural ores are preferred. If siderite is sourced in the form of a finely ground powder, the powder is desirably agglomerated and extruded or otherwise shaped prior to use, except when intended for use in applications such as drilling muds, where the use of siderite powder is recommended without prior agglomeration to form larger particles.

In some cases, merely adding up to about 20 weight percent water to the siderite powder, with mixing, will provided sufficient agglomeration to permit powdered siderite to be extruded into pellets of suitable size or strands that, when dried and subsequently handled, will be friable or easily broken into granules that are satisfactory for use in absorption beds through which sulfur-containing liquids or gases can be passed or circulated for sulfur removal. In some cases, the use of a minor effective amount of a binder, most preferably a cementitious material as further described below may be desirable for use in agglomerating finely divided ferrous carbonate powders.

Although it will be appreciated upon reading this disclosure that ferrous carbonate can be synthesized, the use of ferrous carbonate obtained in naturally occurring siderite mineral ores is preferred for economic reasons. *Hawley's Condensed Chemical Dictionary* (*Twelfth Edition*) reports that siderite ores naturally occur in Vermont, Massachusetts, Connecticut, New York, North Carolina, Pennsylvania, Ohio and Europe.

Extrudates useful in the absorbent bed of the invention can be prepared by mixing powdered siderite with a minor effective amount, such as about 5 weight percent of the total, of a binder such as calcium aluminate cement or another similarly effective material that does not significantly detract from the ability of the siderite to absorb sulfur or sulfur-containing compounds from a gas or liquid stream. A preferred calcium aluminate cement for use in the invention is marketed under the trademark FONDU® by Lafarge Aluminate of Chesapeake, Va. According to a particularly preferred embodiment of the invention, about 5 parts by weight calcium aluminate cement is blended into about 95 parts by weight siderite powder (90% through 100 mesh) to distribute the cement throughout the siderite.

About 20 parts by weight water per 100 parts by weight of blended siderite and cement is desirably admixed with the solids to hydrate the binder and facilitate the formation of larger aggregates, which are then dried to a desired moisture content. Most preferably, the siderite, cement and water mixture is extruded and chopped, such as by use of a rotary pelletizer, or otherwise divided or broken, into extrudates having a diameter of approximately 3/16 inch and a length of approximately 5/16 inch. The extrudates produced from powder as described above are desirably dried at a temperature of about 120° F. for about four hours. Although the required drying time can vary according to the size and dimensions of the pellets, the drying temperature and the humidity of the ambient air, the moisture content of the aggregated solids is desirably reduced to less than about three weight percent during the drying stage.

The absorbent and method disclosed herein are particularly effective for absorbing hydrogen sulfide, mercaptans, dimethyldisulfide and other sulfur compounds from natural gas, light hydrocarbon streams such as NGL, crude oil, acid gas mixtures, carbon dioxide gas and liquid, anaerobic gas, landfill gas, geothermal and other sulfur-containing streams. For most applications, the sulfur-containing fluid to be treated is passed through a bed of the subject absorbent pellets or granules that are disposed inside a vessel such as a cylindrical tower. The amount of absorbent that is needed in the absorbent bed will depend upon many factors such as the sulfur content in the feed, the desired sulfur content in the effluent, the desired lifetime of an absorbent charge, the absorbent particle size, the bed density, the effective surface area of the absorbent particles, the amount of ferrous carbonate in the absorbent that is available to absorb the sulfur-containing compounds, and the temperature, pressure, velocity and residence time of the gas or liquid stream being treated as it passes through the bed. For some applications, such as the treatment of sour gases encountered during well drilling operations, granulated siderite absorbent that passes through a 100 mesh sieve can also be beneficially used by combining it with another material such as drilling mud being pumped into a well.

Although extrudates having dimensions ranging from about 1/16 inch to about 1/4 inch are a particularly preferred form for use of the subject absorbent, it will be appreciated that granules of suitable size can be produced by pulverizing siderite chunks in a hammer mill or by using other commercially available devices well known to those of ordinary skill in the art, and thereafter screening to a suitable particle size range preferably not exceeding about 5/16 inch. Similarly, where siderite powder or synthetically produced ferrous carbonate powder is the starting material, means other than extrusion can also be used for agglomerating or densifying the powder for use in various sulfur removal processes. Such other means include, for example, hydraulically actuated presses or other compaction devices. In most cases, minor effective amounts of a binder and water are desirably added to the powdered siderite or ferrous carbonate to facilitate agglomeration of the individual mineral particles into larger solid bodies, provided that the binder does not too greatly reduce the effective surface area of the absorbent.

Representative Siderite Analysis

A processed siderite composition having a bulk density of 110 pounds per cubic foot, a specific gravity of 3.63 and a particle size of 90% through 100 mesh, has the following analysis:

	wt %
Fe (elemental)	43.00%
$FeCO_3$	86.87
SiO_2	5.50
Al_2O_3	1.30
CaO	0.56
MgO	0.53
S	0.40
Mn	0.35
Cu	0.30
Co	0.02

-continued

	wt %
Cd	0.0041
Pb	0.0001
As	0.00005
Sb	0.00005
Fe_2O_3	<1.0

Sample A

To demonstrate the utility of the invention, a finely divided siderite powder (90% through 100 mesh) was blended with calcium aluminate cement in a ratio of 95 parts siderite to 5 parts cement by weight. Approximately 20 parts by weight water were blended with the siderite and cement mixture, and the mixture was then extruded to produce a plurality of extrudates having a diameter of about 3/16 inch and a length of about 5/16 inch. These extrudates were dried at 120 degrees F. for four hours to a moisture content less than about 3 wt. %.

Sample B

Another siderite material was produced by obtaining chunks of siderite ore approximately 3 to 4 inches in diameter and grinding them to produce granular particles comprising about 90 wt. % ferrous carbonate and ranging in size from about 1/8 inch to about 1/4 inch. Dirt and other contaminants were removed from the granulated siderite using a sieve.

The usefulness of the absorbent materials, when prepared as described above, for removing sulfur from gas and liquid streams containing sulfurous compounds is further described and explained in relation to the examples presented below. All stated inlet and outlet compositions are in parts per million (ppm). Front end sulfurs are stated in ppm of the sulfur-containing compound by weight of the fluid stream. Thiols are stated in ppm of the respective thiol by weight of the fluid stream.

Example 1

A stream of carbon dioxide acid gas was charged at a rate of about 60 mls per minute in an upflow direction through a vertical iron pellet treater containing a bed approximately 8 inches high and 2 inches in diameter of the Sample A extrudates prepared as described above. The treater temperature was 68 deg. F. and the treater pressure was 200 psig. The inlet and outlet compositions of the gas are set forth in Table 1 below:

TABLE 1

Treater					Thiols		
Sample	Front End Sulfurs						1-
Points	COS	H_2S	CS_2	DMDS	Methyl	Ethyl	Propyl
Inlet	7.7	13307.3	0.4	2.4	575.2	481.3	1.3
Outlet	4.1	2.6	1.0	0.7	50.5	17.6	0.3
% Reduction	46.9	99.9	−135	72.1	91.2	96.3	78.4

Example 2

A stream of carbon dioxide acid gas was charged at a rate of about 60 mls per minute in an upflow direction through a vertical H_2S absorbent treater containing a bed approximately 8 inches high and 2 inches in diameter of the Sample B granules prepared as described above. The treater temperature was 68 deg. F. and the treater pressure was 200 psig. The inlet and outlet compositions of the gas are set forth in Table 2 below:

TABLE 2

Treater					Thiols		
Sample	Front End Sulfurs						1-
Points	COS	H_2S	CS_2	DMDS	Methyl	Ethyl	Propyl
Inlet	7.7	13307.3	0.4	2.4	575.2	481.3	1.3
Outlet	4.4	0.2	7.6	20.6	1.5	0.3	0.01
% Reduction	42.8	100	−1780	−765	99.7	100	99.2

Example 3

A stream of natural gas was charged at a rate of about 60 mls per minute in an upflow direction through a vertical iron pellet treater containing a bed approximately 8 inches high and 2 inches in diameter of the Sample A extrudates prepared as described above. The treater temperature was 70 deg. F. and the treater pressure was 500 psig. The inlet and outlet compositions of the gas are set forth in Table 3 below:

TABLE 3

Treater Sample	Front End Sulfurs				Thiols		
Points	COS	H_2S	CS_2	DMDS	Methyl	Ethyl	1-Propyl
Inlet	2.6	93.5	2.8	1.6	90.7	110.3	7.2
Outlet	1.9	0.9	2.2	1.4	6.6	16.9	1.4
% Reduction	25.7	99.0	22.8	11.9	92.7	84.7	80.1

Example 4

A stream of natural gas was charged at a rate of about 60 mls per minute in an upflow direction through a vertical H_2S absorbent treater containing a bed approximately 8 inches high and 2 inches in diameter of the Sample B granules prepared as described above. The treater temperature was 70 deg. F. and the treater pressure was 500 psig. The inlet and outlet compositions of the gas are set forth in Table 4 below:

TABLE 4

Treater Sample	Front End Sulfurs				Thiols		
Points	COS	H_2S	CS_2	DMDS	Methyl	Ethyl	1-Propyl
Inlet	2.6	93.5	2.8	1.6	90.7	110.3	7.2
Outlet	1.8	0.01	2.3	1.1	0.3	0.1	0.01
% Reduction	29	100	16.8	35.1	99.7	99.9	99.9

Example 5

A stream of natural gas was charged at a rate of about 60 mls per minute in an upflow direction through a vertical iron pellet treater containing a bed approximately 8 inches high and 2 inches in diameter of the Sample A extrudates prepared as described above. The treater temperature was 70 deg. F. and the treater pressure was 500 psig. The inlet and outlet compositions of the gas are set forth in Table 5 below:

TABLE 5

Treater Sample	Front End Sulfurs				Thiols		
Points	COS	H_2S	CS_2	DMDS	Methyl	Ethyl	1-Propyl
Inlet	2.6	92.9	2.5	1.8	89.5	102.6	7.0
Outlet	2.2	1.5	1.9	1.3	10.2	17.2	1.5
% Reduction	16.5	98.3	25.1	27.6	88.6	83.2	78.4

Example 6

A stream of natural gas was charged at a rate of about 60 mls per minute in an upflow direction through a vertical H_2S absorbent treater containing a bed approximately 8 inches high and 2 inches in diameter of the Sample B granules prepared as described above. The treater temperature was 70 deg. F. and the treater pressure was 500 psig. The inlet and outlet compositions of the gas are set forth in Table 6 below:

TABLE 6

Treater Sample	Front End Sulfurs				Thiols		
Points	COS	H_2S	CS_2	DMDS	Methyl	Ethyl	1-Propyl
Inlet	2.6	92.3	2.5	1.8	89.5	102.6	7.0
Outlet	1.8	0.01	1.7	1.2	0.1	0.2	0.03
% Reduction	30.3	100	33.3	31.3	99.9	99.8	99.6

Example 7

A stream of natural gas was charged at a rate of about 60 mls per minute in an upflow direction through a vertical iron pellet treater containing a bed approximately 8 inches high and 2 inches in diameter of the Sample A extrudates prepared as described above. The treater temperature was 100 deg. F. and the treater pressure was 500 psig. The inlet and outlet compositions of the gas are set forth in Table 7 below:

TABLE 7

Treater Sample	Front End Sulfurs				Thiols		
Points	COS	H_2S	CS_2	DMDS	Methyl	Ethyl	1-Propyl
Inlet	1.8	225.9	1.7	6.3	126.6	78.1	2.3
Outlet	0.3	0.7	1.6	4.4	94.4	65.3	1.9
% Reduction	81.5	99.7	10.5	29.8	25.4	16.4	14.5

Example 8

A stream of natural gas was charged at a rate of about 60 mls per minute in an upflow direction through a vertical H_2S absorbent treater containing a bed approximately 8 inches high and 2 inches in diameter of the Sample B granules prepared as described above. The treater temperature was 100 deg. F. and the treater pressure was 500 psig. The inlet and outlet compositions of the gas are set forth in Table 8 below:

TABLE 8

Treater Sample	Front End Sulfurs				Thiols		
Points	COS	H_2S	CS_2	DMDS	Methyl	Ethyl	1-Propyl
Inlet	1.8	225.9	1.7	6.3	126.6	78.1	2.3
Outlet	0.5	2.7	0.9	13.2	86.0	58.2	1.7
% Reduction	74.0	98.8	50.2	−111.5	32.1	25.5	24.4

Example 9

A stream of natural gas was charged at a rate of about 60 mls per minute in an upflow direction through a vertical iron pellet treater containing a bed approximately 8 inches high and 2 inches in diameter of the Sample A extrudates prepared as described above. The treater temperature was 130 deg. F. and the treater pressure was 500 psig. The inlet and outlet compositions of the gas are set forth in Table 9 below:

TABLE 9

Treater Sample	Front End Sulfurs				Thiols		
Points	COS	H_2S	CS_2	DMDS	Methyl	Ethyl	1-Propyl
Inlet	1.9	225.2	1.6	6.3	102.7	80.2	2.2
Outlet	0.3	0.6	1.2	2.9	82.7	65.1	1.7
% Reduction	82.6	99.7	25.1	53.0	19.5	18.9	21.9

Example 10

A stream of natural gas was charged at a rate of about 60 mls per minute in an upflow direction through a vertical H_2S absorbent treater containing a bed approximately 8 inches high and 2 inches in diameter of the Sample B granules prepared as described above. The treater temperature was 130 deg. F. and the treater pressure was 500 psig. The inlet and outlet compositions of the gas are set forth in Table 10 below:

TABLE 10

Treater Sample	Front End Sulfurs				Thiols		
Points	COS	H_2S	CS_2	DMDS	Methyl	Ethyl	1-Propyl
Inlet	1.9	225.2	1.7	6.3	102.7	80.2	2.2
Outlet	0.4	6.9	0.7	1.4	62.0	51.4	1.8
% Reduction	78.4	96.9	55.0	77.1	39.7	35.9	16.6

Example 11

A stream of natural gas liquid was charged at a rate of about 40 mls per minute in an upflow direction through a vertical iron pellet treater containing a bed approximately 8 inches high and 2 inches in diameter of the Sample A extrudates prepared as described above. The treater temperature was 52 deg. F. and the treater pressure was 500 psig. The inlet and outlet compositions of the gas are set forth in Table 11 below:

TABLE 11

Treater Sample	Front End Sulfurs				Thiols		
Points	COS	H_2S	CS_2	DMDS	Methyl	Ethyl	1-Propyl
Inlet	6.6	0.01	0.7	0.24	14.9	25.7	18.9
Outlet	6.3	0.01	21.8	1.6	2.0	3.1	2.7
% Reduction	4.8	0.0	−3303	−672.3	86.4	87.8	85.8

Example 12

A stream of natural gas liquid was charged at a rate of about 40 mls per minute in an upflow direction through a vertical iron pellet treater containing a bed approximately 8 inches high and 2 inches in diameter of the Sample A extrudates prepared as described above. The treater temperature was 52 deg. F. and the treater pressure was 500 psig. The inlet and outlet compositions of the gas are set forth in Table 12 below:

TABLE 12

Treater Sample	Front End Sulfurs				Thiols		
Points	COS	H_2S	CS_2	DMDS	Methyl	Ethyl	1-Propyl
Inlet	7.0	0.01	0.7	0.1	20.3	26.1	18.0
Outlet	6.3	0.01	6.5	0.7	0.9	1.8	2.2
% Reduction	9.1	0.0	−866	−763.3	95.5	93.2	87.7

Example 13

A stream of natural gas liquid was charged at a rate of about 40 mls per minute in an upflow direction through a vertical iron pellet treater containing a bed approximately 8 inches high and 2 inches in diameter of the Sample A extrudates prepared as described above. The treater temperature was 60 deg. F. and the treater pressure was 500 psig. The inlet and outlet compositions of the gas are set forth in Table 13 below:

TABLE 13

Treater Sample	Front End Sulfurs				Thiols		
Points	COS	H_2S	CS_2	DMDS	Methyl	Ethyl	1-Propyl
Inlet	7.2	0.62	3.9	0.3	16.3	21.9	17.9
Outlet	6.8	0.01	0.1	0.1	0.7	1.3	1.7
% Reduction	6.1	98.4	97.5	63.0	95.6	93.9	90.3

Example 14

A stream of natural gas liquid was charged at a rate of about 40 mls per minute in an upflow direction through a vertical iron pellet treater containing a bed approximately 8 inches high and 2 inches in diameter of the Sample A extrudates prepared as described above. The treater temperature was 60 deg. F. and the treater pressure was 500 psig. The inlet and outlet compositions of the gas are set forth in Table 14 below:

TABLE 14

Treater Sample	Front End Sulfurs				Thiols		
Points	COS	H_2S	CS_2	DMDS	Methyl	Ethyl	1-Propyl
Inlet	7.2	0.7	3.8	0.34	16.5	21.9	17.9
Outlet	6.8	0.01	6.5	0.1	0.5	1.3	1.6
% Reduction	5.7	98.6	−98.0	72.1	97.0	94.2	91.3

Example 15

A stream of carbon dioxide gas was charged at a rate of about 40 mls per minute in an upflow direction through a vertical iron pellet treater containing a bed approximately 8 inches high and 2 inches in diameter of the Sample A extrudates prepared as described above. The treater temperature was 52 deg. F. and the treater pressure was 500 psig. The inlet and outlet compositions of the gas are set forth in Table 15 below:

TABLE 15

Treater Sample	Front End Sulfurs				Thiols		
Points	COS	H_2S	CS_2	DMDS	Methyl	Ethyl	1-Propyl
Inlet	261.5	201.3	177.7	12.9	199.1	188.8	0.01
Outlet	252.8	0.01	159.3	0.5	0.01	0.01	0.01
% Reduction	3.3	100	10.4	96.3	100	100	0

Example 16

A stream of carbon dioxide gas was charged at a rate of about 40 mls per minute in an upflow direction through a vertical iron pellet treater containing a bed approximately 8 inches high and 2 inches in diameter of the Sample A extrudates prepared as described above. The treater temperature was 52 deg. F. and the treater pressure was 500 psig. The inlet and outlet compositions of the gas are set forth in Table 16 below:

TABLE 16

Treater Sample	Front End Sulfurs				Thiols		
Points	COS	H_2S	CS_2	DMDS	Methyl	Ethyl	1-Propyl
Inlet	259.3	199.9	176.3	12.4	201.5	185.7	0.0
Outlet	248.6	0.01	166.8	0.6	0.01	0.01	0.01
% Reduction	4.1	100	5.4	95.1	100	100	0

Example 17

A stream of carbon dioxide gas was charged at a rate of about 40 mls per minute in an upflow direction through a vertical iron pellet treater containing a bed approximately 8 inches high and 2 inches in diameter of the Sample A extrudates prepared as described above. The treater temperature was 52 deg. F. and the treater pressure was 500 psig. The inlet and outlet compositions of the gas are set forth in Table 17 below:

TABLE 17

Treater Sample	Front End Sulfurs				Thiols		
Points	COS	H_2S	CS_2	DMDS	Methyl	Ethyl	1-Propyl
Inlet	263.1	202.5	178.1	12.7	198.7	185.0	0.01
Outlet	251.3	0.01	164.1	0.3	0.01	0.01	0.01
% Reduction	4.5	100	7.9	97.4	100	100	0

Example 18

A stream of carbon dioxide gas was charged at a rate of about 40 mls per minute in an upflow direction through a vertical iron pellet treater containing a bed approximately 8 inches high and 2 inches in diameter of the Sample A extrudates prepared as described above. The treater temperature was 52 deg. F. and the treater pressure was 500 psig. The inlet and outlet compositions of the gas are set forth in Table 18 below:

TABLE 18

Treater Sample	Front End Sulfurs				Thiols		
Points	COS	H_2S	CS_2	DMDS	Methyl	Ethyl	1-Propyl
Inlet	256.2	193.8	183.6	18.4	178.5	174.9	0.01
Outlet	234.2	0.01	166.6	0.4	0.01	0.01	0.01
% Reduction	8.6	100	9.3	98.1	100	100	0

Example 19

A stream of carbon dioxide gas was charged at a rate of about 40 mls per minute in an upflow direction through a vertical iron pellet treater containing a bed approximately 8 inches high and 2 inches in diameter of the Sample A extrudates prepared as described above. The treater temperature was 52 deg. F. and the treater pressure was 500 psig. The inlet and outlet compositions of the gas are set forth in Table 19 below:

TABLE 19

Treater Sample	Front End Sulfurs				Thiols		
Points	COS	H_2S	CS_2	DMDS	Methyl	Ethyl	1-Propyl
Inlet	5.9	5.1	20.0	27.7	38.0	56.2	7.2
Outlet	4.6	0.01	1.4	0.1	2.3	1.7	0.1
% Reduction	22.0	99.8	93.0	99.5	93.9	97.0	98.0

Example 20

A stream of carbon dioxide gas was charged at a rate of about 40 mls per minute in an upflow direction through a vertical iron pellet treater containing a bed approximately 8 inches high and 2 inches in diameter of the Sample A extrudates prepared as described above. The treater temperature was 52 deg. F. and the treater pressure was 500 psig. The inlet and outlet compositions of the gas are set forth in Table 20 below:

TABLE 20

Treater Sample	Front End SulFurs				Thiols		
Points	COS	H_2S	CS_2	DMDS	Methyl	Ethyl	1-Propyl
Inlet	6.1	5.6	19.6	27.8	38.4	56.4	7.0
Outlet	4.7	0.01	2.2	0.2	2.1	1.4	0.2
% Reduction	23.1	99.8	89.0	99.3	94.4	97.6	97.7

Example 21

A stream of carbon dioxide gas was charged at a rate of about 40 mls per minute in an upflow direction through a vertical iron pellet treater containing a bed approximately 8 inches high and 2 inches in diameter of the Sample A extrudates prepared as described above. The treater temperature was 60 deg. F. and the treater pressure was 500 psig. The inlet and outlet compositions of the gas are set forth in Table 21 below:

TABLE 21

Treater Sample	Front End Sulfurs				Thiols		
Points	COS	H_2S	CS_2	DMDS	Methyl	Ethyl	1-Propyl
Inlet	6.2	24.0	25.9	19.5	43.7	70.4	12.5
Outlet	5.9	0.01	1.7	0.5	0.05	0.8	0.4
% Reduction	4.7	100	93.5	97.3	99.9	98.9	96.8

Example 22

A stream of carbon dioxide gas was charged at a rate of about 40 mls per minute in an upflow direction through a vertical iron pellet treater containing a bed approximately 8 inches high and 2 inches in diameter of the Sample A extrudates prepared as described above. The treater temperature was 60 deg. F. and the treater pressure was 500 psig. The inlet and outlet compositions of the gas are set forth in Table 22 below:

TABLE 22

Treater Sample	Front End Sulfurs				Thiols		
Points	COS	H_2S	CS_2	DMDS	Methyl	Ethyl	1-Propyl
Inlet	6.5	23.9	25.7	19.3	44.2	70.2	12.5
Outlet	6.1	0.01	1.3	0.7	0.01	0.6	0.4
% Reduction	5.4	100	95.0	96.1	100	99.1	96.7

The foregoing examples demonstrate the removal of hydrogen sulfide, thiols (mercaptans), disulfides and carbonyl sulfide from NGL liquid and from the gaseous hydrocarbons and carbon dioxide. Dimethyldisulfide (DMDS) can also be removed by absorption using the compositions and method of the invention. The increase in DMDS observed in some of the examples is believed to be the result of oxidative sweetening reactions in which a small amount of oxygen dissolved in the treated fluid was catalyzed by the iron in the absorbent to promote the oxidation of a small amount of methyl mercaptan to form DMDS plus water.

Increases in the level of carbon disulfide were also noticed in some of the examples. The sulfur analyses were done by sulfur chemiluminescence. Carbon disulfide analysis is very sensitive to the analytical technique used. Since the level of carbon disulfide is very low in the feed, small changes in composition can cause large errors. Errors can also occur because carbon disulfide often contaminates the feed lines, which can thereafter release small amounts of carbon disulfide without notice. When the feed lines were freshly replaced, no reduction in the carbon disulfide content of the fluid stream was measured, and it is believed that little or no carbon disulfide was removed by the absorbent.

The data from Tables 1 and 2 demonstrate that both forms of the absorbent, extrudates (Sample A material) and granules (Sample B material), remove essentially all of the hydrogen sulfide from a CO_2 acid gas stream at ambient temperatures. About half the carbonyl sulfide was removed over both physical forms of the absorbents. The thiols (mercaptans) were also removed at high levels over the granules (99-100%) and over the extrudates (78-96%).

The data from Tables 3-6 demonstrate that 99 to 100% of the hydrogen sulfide can be removed from natural gas at ambient temperatures using the absorbent and method of the invention. The data further demonstrate the removal of 78-100% of the thiols, along with some removal of both carbonyl sulfide and DMDS from the treated fluids.

Comparison of Tables 3-6 (70° F. data) with Tables 7-8 (100° F. data) and Tables 9-10 (130° F. data) shows the effect of temperature. The data demonstrate that 99 to 100% of the hydrogen sulfide is removed at all temperatures using the subject absorbent and method. The thiol removal decreased with increasing temperatures, suggesting that the thiols are desorbing at the higher temperatures. Conversely, the removal of carbonyl sulfide and DMDS increased with increasing temperatures within the ranges tested.

The tests done using a gaseous carbon dioxide feed demonstrate that increasing the pressure from 200 psig (see Tables 1 and 2) to 500 psig (see Tables 15 through 22) appears to aid in the absorption of the thiols. DMDS was 95 to 96% removed at the higher pressure, in comparison to 20 to 72% removal at 200 psig.

NGL liquids tend to be low in hydrogen sulfide concentration. Without competition from hydrogen sulfide, the thiols are removed at levels ranging from 86 to 96% (see Tables 11, 12, 13 and 14). Since oxygen is soluble in this kind of hydrocarbon, the production of DMDS in some the runs may be attributable to the oxidative conversion of small amounts of methyl thiol to DMDS as noted above.

Following use in the iron pellet treater, the Sample A material was removed and examined. The extrudates were uniformly dark from the edge to center after having absorbed 1.2 weight percent sulfur, by weight of the extrudate, from the treated fluid. This observation suggests the occurrence of an exchange reaction during use that causes the sulfur to migrate toward the center of the absorbent. Based upon the composition of the absorbent, the dark (black) color is believed to be ferrous sulfide. The removed extrudates became hot (>135° F.) while sitting out at room temperature, suggesting that the used material is pyrophoric. After sitting out overnight, the used material returned to a lighter brown color more similar to that of the original, pre-use extrudates.

The general conclusion to be drawn from the data presented above is that siderite, whether in the form of granules or in the form of extrudates made from siderite powder, is an excellent absorbent for hydrogen sulfide, thiols (mercaptans), DMDS and carbonyl sulfide in a variety of feed streams. When the reaction conditions favor hydrogen sulfide removal, i.e., higher temperatures and pressures, the thiol removal decreases. The thiols are removed more favorably when the hydrogen sulfide level is low in the feed, at low temperatures, and at high pressures.

Other alterations and modifications of the invention will likewise become apparent to those of ordinary skill in the art upon reading this specification in view of the accompanying drawings, and it is intended that the scope of the invention disclosed herein be limited only by the broadest interpretation of the appended claims to which the inventor is legally entitled.

I claim:

1. An absorbent for sulfur-containing compounds disposed in streams of gas, liquid, or mixed gas and liquid at temperatures ranging from about 52 to about 130° F. and at pressures ranging from about 200 to about 500 psig, the absorbent comprising ferrous carbonate as its principal absorptive component.

2. The absorbent of claim **1**, comprising from about 50 to about 100 weight percent ferrous carbonate.

3. The absorbent of claim **2**, comprising about 95 weight percent ferrous carbonate.

4. The absorbent of claim **2**, further comprising from about 2 to about 10 weight percent of a binder.

5. The absorbent of claim **4**, comprising about 5 weight percent of a binder.

6. The absorbent of claim **1** wherein the ferrous carbonate is in the form of the mineral siderite.

7. The absorbent of claim **6** wherein the siderite is in the form of granules.

8. The absorbent of claim **6** wherein the siderite is in the form of agglomerates.

9. The absorbent of claim **6** wherein the siderite is in the form of extrudates.

10. The absorbent of claim **4** wherein the binder is calcium aluminate cement.

11. The absorbent of claim **7** where the granules have particle sizes ranging between about 1/16 inch and about 5/16 inch.

12. The absorbent of claim **9** wherein the extrudates have a length not exceeding about 5/16 inch.

13. The absorbent of claim **1** in the form of agglomerated and densified powder.

14. The absorbent of claim **1** in the form of particles selected from the group consisting of pellets, prills and spheroids.

15. The absorbent of claim **13** comprising powdered siderite in combination with a binder.

16. The absorbent of claim **15** wherein the binder comprises calcium aluminate.

17. The absorbent of claim **15** comprising from about 50 to about 100 weight percent siderite, from about 2 to about 10 weight percent binder, and a moisture content less than 3 weight percent.

18. The absorbent of claim **15** wherein the powdered siderite has a particle size of about 100 mesh.

19. The absorbent of claim **13**, made by blending powdered siderite and calcium aluminate cement in the presence of water, and thereafter extruding, sizing and drying the resultant product.

20. A method for making an absorbent that is useful for removing sulfur-containing compounds disposed in streams of gas, liquid, or mixed gas and liquid by providing from about 50 to about 100 parts by weight of ferrous carbonate having a particle size of about 100 mesh, by blending with the ferrous carbonate from about 2 parts by weight to about 10 parts by weight cementitious binder and from about 15 to about 25 parts by weight water, by extruding the blended ferrous carbonate, cementitious binder and water to produce an extrudate of desired length, and by thereafter drying the extrudate to a moisture content less than 3 weight percent.

21. The method of claim **20** wherein the ferrous carbonate is siderite.

22. The method of claim **20** wherein the cementitious binder comprises calcium aluminate.

23. The method of claim **21**, wherein about 5 parts by weight cementitious binder and about 20 parts by weight water are blended with about 95 parts by weight siderite powder.

24. The method of claim **23** wherein the siderite powder has a particle size of about 100 mesh.

25. A method for absorbing sulfur-containing compounds disposed in a stream of gas, liquid, or mixed gas and liquid at temperatures ranging from about 52 to about 130° F. and at pressures ranging from about 200 to about 500 psig by providing an absorbent principally comprising ferrous carbonate as its principal absorptive component and by contacting the ferrous carbonate with the stream.

26. The method of claim **25** wherein the ferrous carbonate is siderite.

27. The method of claim **26** wherein the absorbent is in the form of pellets made from a blend of powdered siderite and a cementitious binder, together with sufficient water to hydrate the cement.

28. The method of claim **26** wherein the pellets comprise from about 70 to about 100 weight percent siderite and from about 2 to about 10 weight percent cementitious binder.

29. The method of claim **27** wherein the cementitious binder is calcium aluminate cement.

30. The method of claim **27** wherein the pellets are extruded.

31. The method of claim **27** wherein the pellets are dried to a moisture content less than 3 weight percent.

32. The method of claim **25** wherein the sulfur-containing compounds are selected from the group consisting of hydrogen sulfide, carbonyl sulfide, organic disulfides and mercaptans.

33. The method of claim **27** wherein the pellets are arranged in a bed.

34. The method of claim **33** wherein the stream comprises a fluid selected from the group consisting of natural gas, natural gas liquids, light light hydrocarbons, crude oil, acid gas mixtures, gaseous carbon dioxide, anaerobic gas, landfill gas, and geothermal fluids.

35. The method of claim **25** wherein the stream comprises sour gas inside a well bore and wherein the ferrous carbonate is finely divided and is distributed in a drilling mud that is circulated through the well bore.

36. The absorbent of claim **1** wherein the sulfur-containing compounds are selected from the group consisting of hydrogen sulfide, carbonyl sulfide, organic disulfides and mercaptans.

37. The absorbent of claim **1** wherein the stream comprises a fluid selected from the group consisting of natural gas, natural gas liquids, light hydrocarbons, crude oil, acid gas mixtures, gaseous carbon dioxide, anaerobic gas, landfill gas, and geothermal fluids.

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